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# Study on Oxidation of Chalcones with Lead Tetraacetate and Manganic Acetate

Kazu Kurosawa and Junko Higuchi

*Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami-machi, Kumamoto*

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2′-Hydroxychalcones were oxidized with lead tetraacetate and manganic acetate to give *trans*- and *cis*-aurones, together with substituted benzoic acids and cinnamic acid. In the oxidation, 2′-benzyloxy-4,4′-dimethoxychalcone gave 2-acetoxy-1-(2′-benzyloxy-4′-methoxy)phenyl-3-(4′-methoxy)phenylpropane-1,3-dione and *erythro*-2,3-diacetoxy-1-(2′-benzyloxy-4′-methoxy)phenyl-3-(4′-methoxy)phenylpropan-1-one. Structures of the products were elucidated spectrometrically and confirmed by syntheses.

Several papers[1–4] have been published on the oxidation of various organic compounds with manganic acetate. In a previous communication,[5] it was reported that 2′-hydroxychalcones (Ia–i) were oxidized with manganic acetate to give aurones (IIa–i). In some cases,[3,4] however, it was shown that under certain conditions the reagent has a strong similarity to lead tetraacetate.[6] We therefore carried out the oxidation of Ia–i with lead tetraacetate and also examined the oxidation with manganic acetate more in detail. We wish to report both results in this paper.

When 2′-hydroxychalcones (Ia–c) were oxidized with either manganic acetate or lead tetraacetate in acetic acid, several compounds were isolated (Table 1). From mother liquors of the main products aurones (IIb and IIc), compounds IIIb and IIIc, respectively, were separated by successive thin layer chromatography and were found to be isomers of IIb and IIc from the following evidences. IR spectra of IIIb and IIIc showed absorptions at 1676—1679 cm$^{-1}$ which are slightly lower than those of IIa, IIb, and IIc (1700 cm$^{-1}$) (Table 2). In 60 MHz NMR spectra of IIa, IIb, IIc, IIIb, and IIIc (Table 3), the difference was shown in a signal corresponding to H$_{2'}$ and H$_{6'}$/ or H$_{6'}$. The signals of H$_{2'}$ and H$_{6'}$ of IIIb and H$_{6'}$ of IIIc appeared at $\delta$8.29 and 8.77, respectively, rather lower field shifts as compared with those of IIb ($\delta$ 8.06) and IIc ($\delta$ 8.12). The cause of the shifts could be ascribed to the anisotropic effect of a carbonyl group. Thus, the NMR spectra indicated that IIa, IIb, and IIc have a *trans*-configuration with respect to the carbonyl and the phenyl groups, and IIIb and IIIc have a *cis*-configuration. Their UV spectra showed a characteristic absorption pattern, *viz.*, the *trans*-isomer (IIa–c) has an absorption maximum at a longer wavelength (376—392 nm) and the *cis*-isomer at a shorter wavelength (350—352 nm) (Table 2).

Three acidic compounds were isolated and they were found to be a 2-hydroxybenzoic acid (IV), a

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[1] T. Aratani and M. J. S. Dewer, *J. Amer. Chem. Soc.*, **88**, 5479 (1966).

[2] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **91**, 138 (1969).

[3] J. B. Bush, Jr. and H. Finkbeiner, *ibid.*, **90**, 5903 (1968).

[4] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **90**, 5905 (1968).

[5] K. Kurosawa, This Bulletin, **42**, 1456 (1969).

[6] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **90**, 2706 (1968).

TABLE 1. OXIDATION OF CHALCONES

| Chalcone[6] | Reagent | Reaction conditions |  | Aurone[6] |  | Product (yield, %), mp (°C) |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Mole ratio of I and Reagent | Time (min) | *trans-* | *cis-* | Acid |  |  | Aldehyde | Ketone |  |
| Ia | $Pb(OAc)_4$ | 1 : 1.5 | 30 | IIa(20)<br>137 |  |  | V(0.52)<br>184 | VIa[8](1.9)<br>170 |  |  |  |
| Ia | $Mn(OAc)_3$ | 1 : 3 | 25 | IIa(32)<br>137 |  | IVa(2.8)<br>149 | trace | VIa(0.56)<br>170 |  |  |  |
| Ib | $Pb(OAc)_4$ | 1 : 1.5 | 30 | IIb(33)<br>133 | IIIb(0.52)<br>163—164 |  | V(1.3)<br>184 | VIa(0.38)<br>170 |  |  |  |
| Ib | $Mn(OAc)_3$ | 1 : 3 | 20 | IIb(30)<br>133 | IIIb(0.55)<br>163—164 | IVb[7](4.0)<br>150 |  |  |  |  |  |
| Ic | $Pb(OAc)_4$ | 1 : 1.5 | 30 | IIc(48)<br>138[a] |  | IVb(1.4)<br>150 |  | VIc[9](1.2)<br>168 |  |  |  |
| Ic | $Mn(OAc)_3$ | 1 : 3 | 30 | IIc(53)<br>138[a] | IIIc(0.82)<br>143—144 | IVb(2.2)<br>150 |  |  |  |  |  |
| Id | $Pb(OAc)_4$ | 1 : 1.5 | 30 | IId(35)<br>190 |  |  |  |  |  |  |  |
| Ie | $Pb(OAc)_4$ | 1 : 1.5 | 30 | IIe(25)<br>182 |  |  |  |  |  |  |  |
| If | $Pb(OAc)_4$ | 1 : 1.5 | 30 | IIf(30)<br>145 |  |  |  |  |  |  |  |
| Ig | $Pb(OAc)_4$ | 1 : 1.5 | 30 | IIg(20)<br>178 |  |  |  |  |  |  |  |
| Ih | $Pb(OAc)_4$ | 1 : 1.5 | 30 | IIh(35)<br>186 |  |  |  |  |  |  |  |
| Ii | $Pb(OAc)_4$ | 1 : 1.5 | 30 | IIi (37)<br>184 |  |  |  |  |  |  |  |
| Ij | $Pb(OAc)_4$ | 1 : 2 | 450 |  |  | IVj (2.3)<br>101—102 | V(4.6)<br>184 |  | VII(5.0) | VIII(6.0)<br>155—156 | IX (5.5)<br>164—166 |
| Ij | $Mn(OAc)_3$ | 1 : 4 | 480 |  |  | IVj (7.0)<br>101—102 | V(2.1)<br>184 |  | VII(9.0) | VIII(8.3)<br>155—156 | IX (3.5)<br>164—166 |

a) This was previously reported as 129°C, but has been corrected.

TABLE 2. IR AND UV SPECTRAL DATA FOR IIa, IIb, IIc, IIIb, AND IIIc

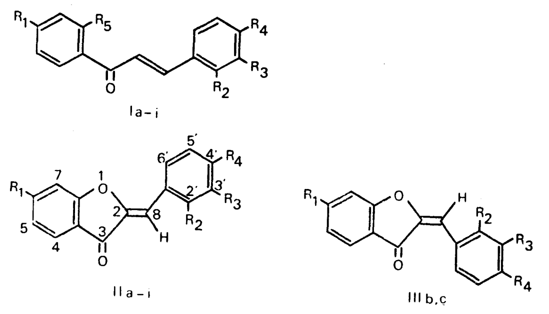
| Compound | $\nu_{max}$ ($cm^{-1}$) |  | $\lambda_{max}$ (nm) (log $\varepsilon$) |  |  |
|---|---|---|---|---|---|
|  | C=O | C=C |  |  |  |
| IIa | 1700 | 1640 | 255(4.18) | 333(4.13) | 392(4.45) |
| IIb | 1700 | 1647 | 253(4.11) |  | 376(4.49) |
| IIIb | 1676 | 1637 | 256(4.15) | 350(4.36) | 394(inf) (4.25) |
| IIc | 1700 | 1645 | 261(4.07) |  | 382(4.42) |
| IIIc | 1679 | 1637 | 263(4.12) | 352(4.29) | 369(inf) (4.19) |

inf; inflection

TABLE 3. NMR SPECTRAL DATA FOR IIa, IIb, IIc, IIIb, AND IIIc ($\delta$ VALUE AT 60 MHz)

| Compound | $H_4$[a] | $H_5$[a] | $H_6$ | $H_7$[a] | $H_8$ |  | $H_{2',6'}$/or $H_{6'}$[b] |  | $H_{3',5'}$/or $H_5$[b] |  | $OCH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | *trans* | *cis* | *trans* | *cis* | *trans* | *cis* |  |
| IIa | 7—8(4H) |  |  |  | 7.06 |  | 8.06 |  | 7.14 |  | 3.95(3H) |
| IIb | 7.89 | 6.92 | — | 6.92 | 6.97 |  | 8.06 |  | 7.13 |  | 3.95(3H)<br>4.02(3H) |
| IIIb | 7.72 | 6.74 | — | 6.67 |  | 6.90 |  | 8.29 |  | 7.00 | 3.90(3H)<br>3.87(3H) |
| IIc | 7.78 | 6.80 | — | 6.80 | 7.32 |  | 8.12 |  | 6.86 |  | 4.02(3H)<br>3.99(9H) |
| IIIc | 7.79 | 6.77 | — | 6.71 |  | 7.37 |  | 8.77 |  | 6.86 | 4.00(6H)<br>3.95(6H) |

a) $J_{4,5}=8.5$ Hz, $J_{5,7}=2$ Hz, $J_{2',3'}=J_{5',6'}=8.5$ Hz, analysed as an AB system.
b) $J_{5',6'}=8.5$ Hz.



a $R_1=R_2=R_3=H$, $R_4=OCH_3$, $R_5=OH$
b $R_2=R_3=H$, $R_1=R_4=OCH_3$, $R_5=OH$
c $R_1=R_2=R_3=R_4=OCH_3$, $R_5=OH$
d $R_1=R_2=H$, $R_3=R_4=OCH_2O$, $R_5=OH$
e $R_1=R_3=H$, $R_2=R_4=OCH_3$, $R_5=OH$
f $R_1=H$, $R_2=R_3=R_4=OCH_3$, $R_5=OH$
g $R_2=H$, $R_1=OCH_3$, $R_3=R_4=OCH_2O$, $R_5=OH$
h $R_1=R_3=R_4=OCH_3$, $R_2=H$, $R_5=H$
i $R_1=R_2=R_4=OCH_3$, $R_3=H$, $R_5=OH$
j $R_1=R_4=OCH_3$, $R_2=R_3=H$, $R_5=OCH_2Ph$

Fig. 1.

benzoic acid (V) and a cinnamic acid (VI). They were identified with authentic samples by their IR spectra.

It was reported recently[10] that the reaction of of chalcones with thallium acetate gave a product in which a skeletal rearrangement took place. This prompted us to investigate the oxidation of 2′-benzyloxy-4,4′-dimethoxychalcone (Ij)[11] with lead tetraacetate and manganic acetate. With both reagents, identical products IVj, V, VII, VIII, and IX were obtained (Table 1).

Product (VIII), $C_{26}H_{24}O_7$ (analysis and mass spectrum), mp 155—156°C, was isolated from chloroform extract of the reaction mixture by preparative tlc and recrystallization. The IR spectrum of VIII ($\nu_{max}$ 1750, 1250, and 1675 cm$^{-1}$) suggested the presence of an acetoxyl group and an aroyl group. The NMR spectrum (100 MHz) of VIII indicated the presence of a *p*-methoxybenzoyl group {δ 6.68(d, 2H), δ 7.61 (d, 2H) (AA′BB′ system, $J_{AB}=J_{A'B'}=9$ Hz), and δ 3.64 (s, 3H)}, a 2-benzyloxy-4-methoxybenzoyl group δ 7.09 (broad s, 5H), δ 4.70 (d, 1H) and δ 4.82 (d, 1H) (AB system, $J=12.0$ Hz), δ 6.26 (d, 1H), δ 6.46 (dd, 1H) and δ 7.92(d, 1H)(ABX system, $J_{AB}=2$ Hz, $J_{AX}=0$ and $J_{BX}=9$ Hz), and δ 3.73(s, 3H)}, and an acetoxyl group {δ 2.08(s, 3H)}. This spectroscopic evidence indicated that product (VIII) is 2-acetoxy-1-(2′-benzyloxy-4′-methoxy)phenyl-3-(4′-methoxy)phenylpropane-1,3-dione.

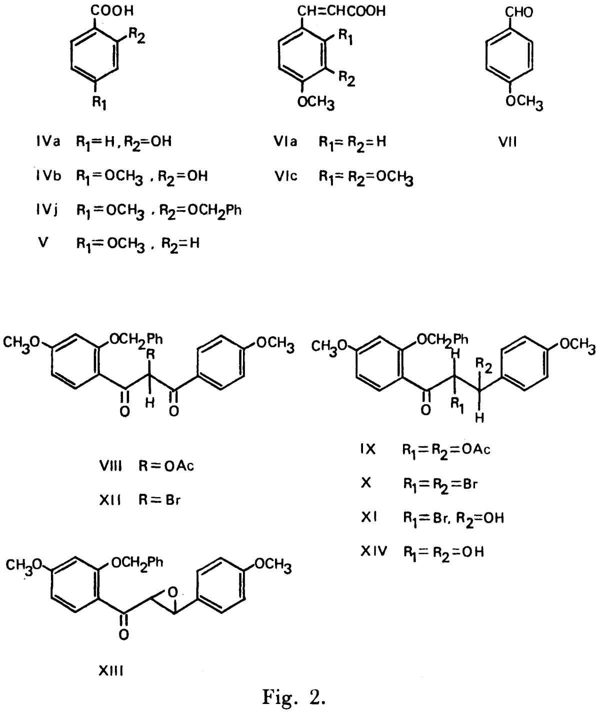
Product (IX), $C_{28}H_{28}O_8$ (analytical and mass spectrum), mp 164—166°C, was isolated also from the chloroform extract. The IR spectrum of IX indicated the presence of an acetoxyl and a benzoyl groups (1745 and 1250, and 1675 cm$^{-1}$, respectively). The NMR spectrum (100 MHz) of IX indicated the presence of a *p*-methoxyphenyl group {δ 6.80(d, 2H), δ 6.58 (d, 2H) (AA′BB′ system, $J_{AB}=J_{A'B'}=9$ Hz) δ 3.68(s, 3H)}, a 2-benzyloxy-4-methoxybenzoyl group {δ 7.3—7.6(m, 5H), δ 5.18(s, 2H), δ 6.52(d, 1H), δ 6.50(dd, 1H) and δ 7.76(d, 1H)(ABX system, $J_{AB}=2.5$, $J_{AX}=0$, and $J_{BX}=9.4$ Hz), δ 3.78(s, 3H)}, two acetoxyl groups {δ 1.92(s, 3H) and δ 2.02(s, 3H)}, and a CH=CH unit{δ 6.28 (d, 1H), and δ 6.36(d, 1H)(AB system, $J=3.0$ Hz)}. All the spectroscopic evidence showed that the product (IX) has a structure of 2,3-diacetoxy-1-(2′-benzoyloxy-4′-methoxy)phenyl-3-(4′-methoxy)phenylpropan-1-one (IX).

The third product isolated from the chloroform extract was found to be anisaldehyde (VII), being identified with an authentic sample by IR spectra.

The fourth product, mp 184°C, was isolated by sodium bicarbonate extraction of the chloroform extract and was proved to be anisic acid (V). This was confirmed on the mixed melting point test with an authentic sample.

The fifth product, mp 100—101°C, was found to be 2-benzyloxy-4-methoxybenzoic acid(IVj) by its NMR spectrum(60 MHz) {δ 7.53(s, 5H), δ 5.32(s, 2H), δ 3.88(s, 3H), δ 6.65(d, 1H), δ 6.70(dd, 1H) and δ 8.22 (d, 1H) (ABX system, $J_{AB}=2$, $J_{AX}=0$, and $J_{BX}=8.5$ Hz), and δ 12.0(s, 1H)}.

The structures of VIII and IX were finally confirmed by syntheses.



IVa $R_1=H$, $R_2=OH$
IVb $R_1=OCH_3$, $R_2=OH$
IVj $R_1=OCH_3$, $R_2=OCH_2Ph$
V $R_1=OCH_3$, $R_2=H$
VIa $R_1=R_2=H$
VIc $R_1=R_2=OCH_3$
VII
VIII R=OAc
XII R=Br
IX $R_1=R_2=OAc$
X $R_1=R_2=Br$
XI $R_1=Br$, $R_2=OH$
XIV $R_1=R_2=OH$
XIII

Fig. 2.

A chalcone dibromide (X), mp 163—165°C, obtained from Ij, was treated with wet acetone.[12] This yielded a bromohydrin (XI), mp 129—130°C. XI was oxidized with chromic acid to a diketone (XII), mp 80—82°C. XII was then heated with sodium acetate in acetic acid to give an acetate. The acetate has a melting point and IR spectrum identical with those of VIII.

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[7] "Beilsteins Handbuch der Organischen Chemie," Vol. 10, p. 379.

[8] *ibid.*, Vol. 10, 298.

[9] *ibid.*, Vol. 10, 508.

[10] W. D. Ollis, K. L. Ormand, *J. Chem. Soc., C,* **1970**, 119.

[11] W. D. Ollis, K. L. Ormand, B. T. Redman, R. J. Roberts, and I.O. Sutherland, *ibid.*, **1970**, 125.

[12] M. G. Marathey, *J. Org. Chem.*, **20**, 563 (1955).

IX was synthesized as follows. The chalcone epoxide (XIII), mp 93°C, was treated with aqueous acetic acid and the resulting glycol (XIV), mp 134—135°C, was acetylated with acetic anhydride in pyridine. This acetate was found to be identical with product (IX). It is also shown by this synthesis that IX has an *erythro* diacetoxy configuration as a *trans*-chalcone epoxide is hydrolysed to a glycol by $S_N2$ mechanism and this makes a *trans* addition to a *trans* double bond.

Thus, the reaction of manganic acetate and lead tetraacetate with chalcone proceeded in a similar way to each other, but differed from the reaction of thallium acetate.[10] Rearranged products have not been isolated. It was also shown that the reaction takes place differently from those of a substituted styrene and a compound having an isolated double bond, which gave a lactone[3,4,6] and a 1,2-diacetate,[13] respectively. It can be said that the carbonyl group must have a significant influence in the oxidation of the chalcone. This was illustrated by the formation of the diketone (VIII), which seemed to be the first example. It seems unlikely that product (IX) is an intermediate in the formation of VIII as the former is not reactive with manganic acetate.

Table 4. Analysis of new compounds

| Compound | Formula | Found | | Calcd | |
|---|---|---|---|---|---|
| | | C% | H% | C% | H% |
| IIc | $C_{19}H_{18}O_6$ | 66.83 | 5.38 | 66.66 | 5.30 |
| IIf | $C_{18}H_{16}O_5$ | 69.23 | 5.20 | 69.22 | 5.16 |
| IIi | $C_{18}H_{16}O_5$ | 69.28 | 5.26 | 69.22 | 5.16 |
| IIIb | $C_{17}H_{14}O_4$ | 72.45 | 5.03 | 72.33 | 5.00 |
| IIIc | $C_{19}H_{18}O_6$ | 66.42 | 5.40 | 66.66 | 5.30 |
| IVj | $C_{15}H_{14}O_4$ | 69.62 | 5.48 | 69.75 | 5.46 |
| VIII | $C_{26}H_{24}O_7$ | 69.65 | 5.53 | 69.63 | 5.39 |
| IX | $C_{28}H_{28}O_8$ | 68.43 | 5.85 | 68.28 | 5.73 |
| X | $C_{24}H_{22}O_4Br_2$ | 53.80 | 4.33 | 53.96 | 4.15 |
| XI | $C_{24}H_{23}O_5Br$ | 60.88 | 4.96 | 61.16 | 4.92 |
| XII | $C_{24}H_{21}O_5Br \cdot 1/3\ C_6H_6$ | 62.80 | 4.80 | 63.04 | 4.68 |
| XIII | $C_{24}H_{22}O_5$ | 73.96 | 5.81 | 73.83 | 5.68 |
| XIV | $C_{24}H_{24}O_6$ | 70.38 | 6.03 | 70.57 | 5.92 |

## Experimental

All NMR spectra were recorded for deuteriochloroform solutions with a JEOL JNM-MH-100 and a JNM-MH-60 spectrometers with tetramethylsilane as an internal standard; IR spectra were recorded for chloroform solution with a JASCO DS 403G grating spectrometer; UV spectra were obtained for methanol solutions with a Hitachi EPS-3T spectrophotometer. Preparative and analytical tlc were carried out with a Wakogel BlO. Melting points were determined with a Yanagimoto micro melting point apparatus and uncorrected.

Lead tetraacetate and manganic acetate were prepared according to references.[14,15]

*Reaction of Lead Tetraacetate with Chalcones(Ia—i).* Chalcone (1 mmol), dissolved in acetic acid (15 m*l*) was heated with lead tetraacetate (1.5 mmol) at 100°C for 30 min. After removal of the acetic acid *in vacuo*, the resulting solid was treated with 2 N sulfuric acid (10 m*l*) and then extracted with chloroform (20 m*l*). The chloroform layer was separated from the aqueous solution and then evaporated. The residue was dissolved in a small amount of chloroform and separated on tlc (10 g×5) with chloroform as an eluent. The crude aurone was recrystallized from ethanol.

*Reactions of Lead Tetraacetate and Manganic Acetate with Chalcones(Ia—c) in a Large Scale.* Chalcone (20 mmol) was oxidized as above with lead tetraacetate (30 mmol) or manganic acetate (60 mmol) and the products were separated on alumina (Wako, 100 g) with chloroform as an eluent. *cis*-Aurone was separated from a *trans*-aurone by repeated tlc and recrystallization from ethanol. Sodium bicarbonate extraction of the chloroform solution yielded a mixture of carboxylic acids (IV, V and VI), which were separated by fractional recrystallization from water.

*Reaction of Manganic Acetate with 2′-Benzyloxy-4,4′-dimethoxychalcone(Ij).*[11] Ij (2 mmol) was dissolved in acetic acid (20 m*l*) containing acetic anhydride (1 m*l*) and then heated with manganic acetate (8 mmol) at 100°C for 8 hr. After removal of the acetic acid, the resulting mixture was hydrolyzed with 2 N sulfuric acid and then extracted with chloroform. The chloroform layer was washed with aqueous sodium bicarbonate. The chloroform being removed, the resulting liquid was chromatographed on preparative tlc (35 g×5) effected with chloroform. From a band running just below Ij, product (VIII) was obtained and recrystallized from ethanol to give colorless plates, mp 155—156°C. From a slow running band, product (IX) was separated after recrystallization from ethanol as colorless needles, mp 164—166°C. From a band just above Ij, colorless liquid was isolated and identified as anisaldehyde (VII) on comparison of its IR spectrum with that of an authentic sample. Upon acidification of the sodium bicarbonate extract, two acids, IVj and V were obtained after recrystallization from water.

*Reaction of Lead Tetraacetate with Ij.* Ij (2 mmol) was oxidized with lead tetraacetate (4 mmol) in acetic acid (20 m*l*) at 100°C for 7.5 hr. Working up in a manner as described above, products (IVj, V, VII, VIII, and IX) were isolated.

*1-(2′-Benzyloxy-4′-methoxy)phenyl-2,3-dibromo-3-(4′-methoxy)-phenylpropan-1-one(X).* Ij (3.74 g) in carbon disulfide (50 m*l*) was treated with bromine (1.6 g) at 0°C for 15 min. The precipitates were collected and recrystallized from benzene to give microcrystals, mp 163—165°C (3.54 g, 67%).

*1-(2′-Benzyloxy-4′-methoxy)phenyl-2-bromo-3-hydroxy-3-(4′-methoxy)phenylpropan-1-one(XI).* X (3.00 g) was treated with 60% aqueous acetone (30 m*l*) under reflux for 15 min. After removal of the acetone, the aqueous solution was extracted with benzene. Benzene was removed and the resulting liquid was allowed to crystallize from a small amount of benzene. Recrystallization of the crude product from the same solvent yielded colorless cubes, mp 129—130°C, (1.22 g, 46%).

*1-(2′-Benzyloxy-4′-methoxy)phenyl-2-bromo-3-(4′-methoxy)-phenylpropane-*1,3*-dione(XII).* To XI (412 mg) in acetic acid (10 m*l*), was added chromic acid (246 mg) in acetic acid (25 m*l*) at room temperature and the mixture was warmed on a steam bath for 2.5 min. The reaction mix-

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13) K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York and London (1965), p. 335.

14) L. F. Audrieth, "Inorganic Syntheses," Vol. 3, McGraw-Hill Co. Inc. (1950), p. 47.

15) P. J. Andrulis, Jr., M. J. S. Dewer, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, **88**, 5473 (1966).

ture was treated with 2 N sulfuric acid (100 m*l*) and then extracted with chloroform. After removal of the chloroform, the resulting liquid was allowed to crystallize from benzene. Recrystallization of the crude product from benzene gave colorless microcrystals, mp 80—82°C, (199 mg, 54%).

*2-Acetoxy-1-(2′-benzyloxy-4′-methoxy)phenyl-3-(4′-methoxy)phenylpropane-1,3-dione (VIII).* XII (112 mg) was treated with a mixture of anhydrous sodium acetate (500 mg) and acetic acid (2 m*l*) under reflux for 7.5 hr. The reaction mixture was treated with 2 N sulfuric acid and then extracted with chloroform. The chloroform layer was concentrated and separated on silica gel (10 g×3) with chloroform as an eluent. From appropriate band, a crude material was separated and recrystallized from ethanol to give colourless plates, mp 154—155°C, (30 mg, 28%).

*2′-Benzyloxy-4,4′-dimethoxychalcone Epoxide (XIII).* To a mixture of the chalcone(Ij) (1 g), acetone (20 m*l*) and methanol (10 m*l*), and 2 N sodium hydroxide (2.0 m*l*) was added 30% hydrogen peroxide (2.5 m*l*) at 50°C during a period of 50 min. The reaction mixture was poured into ice water and extracted with chloroform. After removal of the chloroform, the resulting liquid was allowed to crystallize from ethanol. This yielded colorless microcrystals, mp 93°C, (49%).

*1-(2′-Benzyloxy-4′-methoxy)phenyl-2,3-dihydroxy-3-(4′-methoxy)-phenylpropan-1-one(XIV).* XIII (248 mg) was dissolved into a mixture of acetone (25 m*l*) and 10% acetic acid (25 m*l*) and kept at room temperature for 16 hr. The mixture was diluted with water and the precipitates were collected. Recrystallization of the crude product from ethanol gave colorless needles, mp 134—135°C, (117 mg, 45%).

*2,3-Diacetoxy-1-(2′-benzyloxy-4′-methoxy)phenyl-3-(4′-methoxy)-phenylpropan-1-one(IX).* XIV (117 mg) was treated with a mixture of acetic anhydride (0.5 m*l*) and pyridine (1 m*l*) at 0°C for 18 hr. The reaction mixture was poured into ice water and the precipitates were collected. Recrystallization of the precipitates from ethanol gave colorless needles, mp 164—166°C, (52 mg, (37%).

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